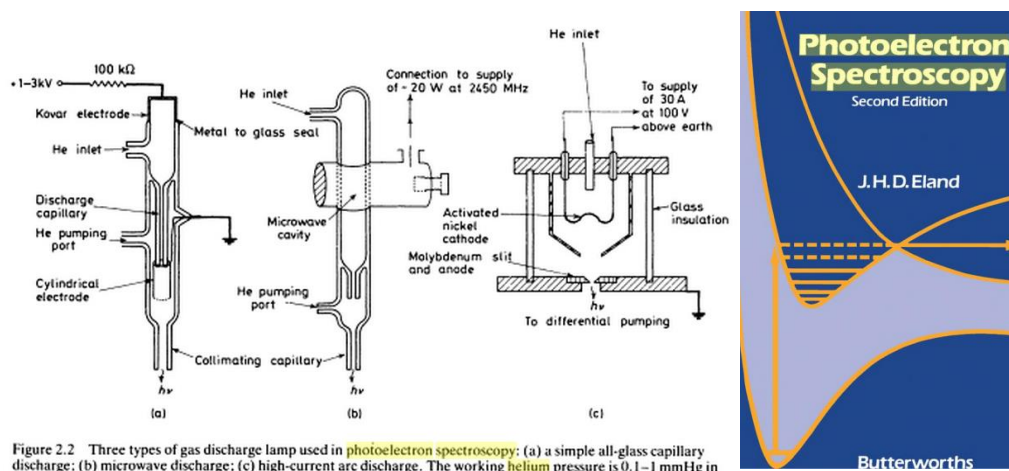


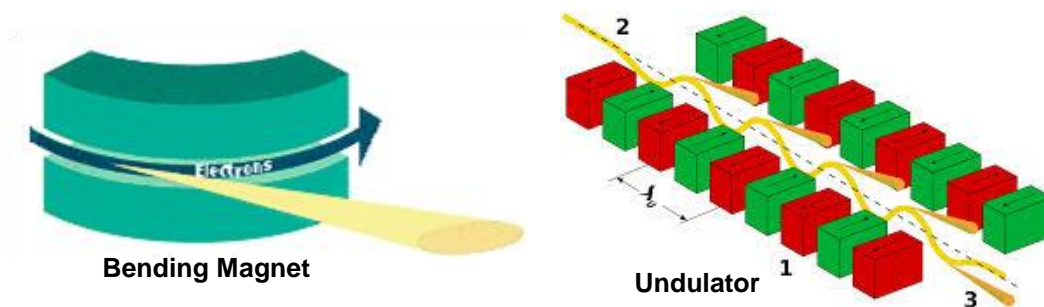
## Photoemission: a technique to determine energy bands and density of states

The photoelectric effect, i.e., the emission of electrons from a surface as a result of absorption of a photon is one of the most powerful tools to investigate the electronic properties of surfaces. In practice photoelectron spectroscopy (PS) techniques have received different names depending on the energy of the photons utilized. Ultraviolet photons, such as those obtained from discharge gas lamps of  $\text{H}_2$ , He and other gases give rise to the UPS or ultraviolet photoemission spectroscopy. Helium gas is used often for that purpose. It produces two narrow UV lines of photons at 21.2 and 40.8 eV, called He-I and He-II lines. Since He-II is due to excited He, it is produced most intensely by lowering the gas pressure, so that the excited He has a long lifetime (which is determined by the collision rate with other He atoms). The lamps have a small orifice communicated with the high vacuum chamber through a differentially pumped stage.

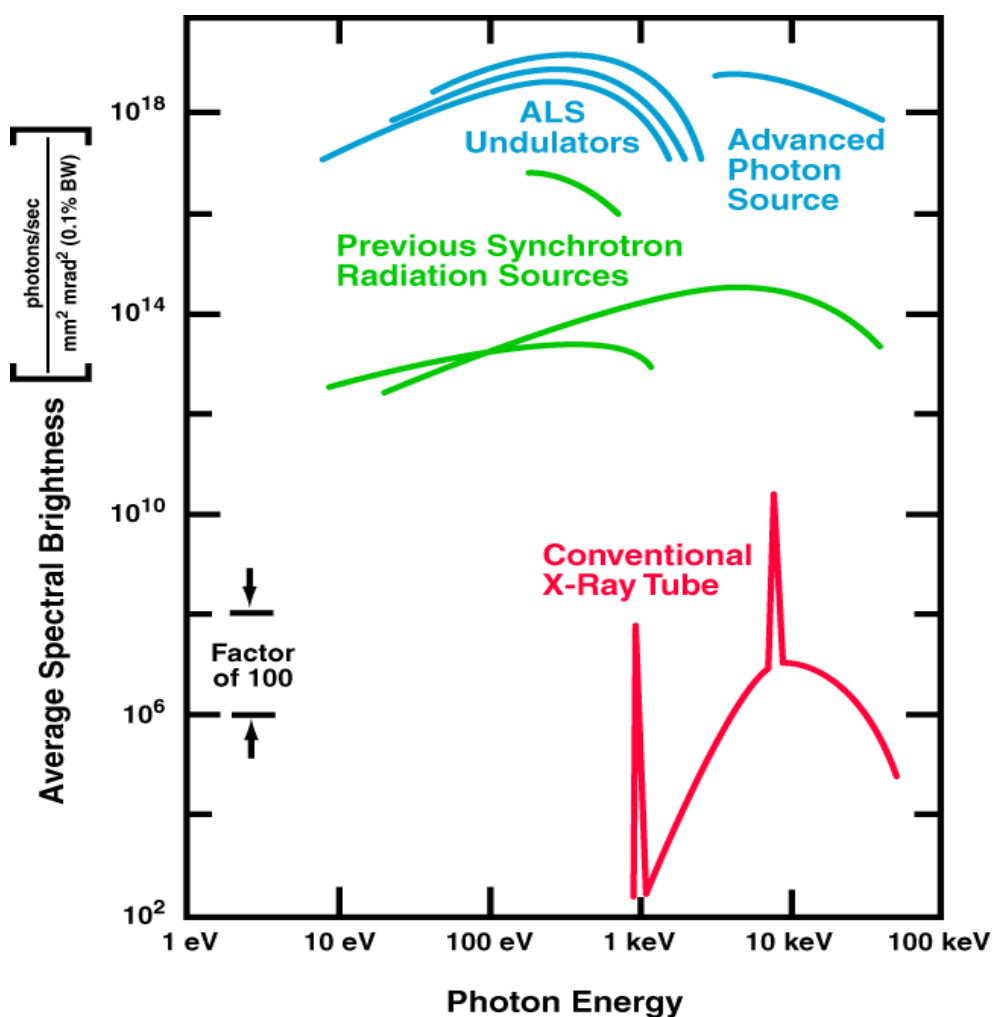


Another popular range of photon energies is around 1200–1500 eV. Soft X-ray photons of this kind are used in many commercial instruments. They are produced by high energy electron bombardment of  $\text{Al K}\alpha$  (=1486.6 eV) and  $\text{Mg K}\alpha$  (=1253.6 eV) anodes, that must be kept refrigerated by cooling water to avoid melting.

Nowadays, with the availability of intense and continuous wavelength X-ray sources, in the synchrotron facilities, one can choose the energy of the photons. These sources provide, in addition to the high intensity and brilliance, polarization, with the E vector in the plane of the electron synchrotron orbit. Two types of devices are inserted in the ring: Bending magnets and Undulators. The first is needed to curve the electron trajectory inside the ring at the corners of the polygonal ring. The radiation is emitted tangential to the curved trajectory. The undulators are inserted in the straight sections of the ring and consist of an array of magnets with north and south poles arranged such that the electrons are forced to follow an oscillatory trajectory, with light being emitted at each turning point in the trajectory. The intensity emitted by undulators can be up to 1000 times higher than that of bending magnets. In addition the polarization can be changed by moving the magnet array to rotate the electron trajectory path.



The graph shows the intensity available in the ALS, the Advanced Light Source of Berkeley. As can be seen, several orders of magnitude higher photon fluxes are achieved than with conventional sources. Several new photoelectron techniques have been made possible with the new facilities, including EXAFS and NEXAFS which will be discussed below.



## Photoemission, secondary emission and density of states

The kinetic energy of the excited electron arising from an initial state of binding energy  $E$  (relative to the Fermi level) is:

$$E_{kin} = h\nu - E - \phi$$

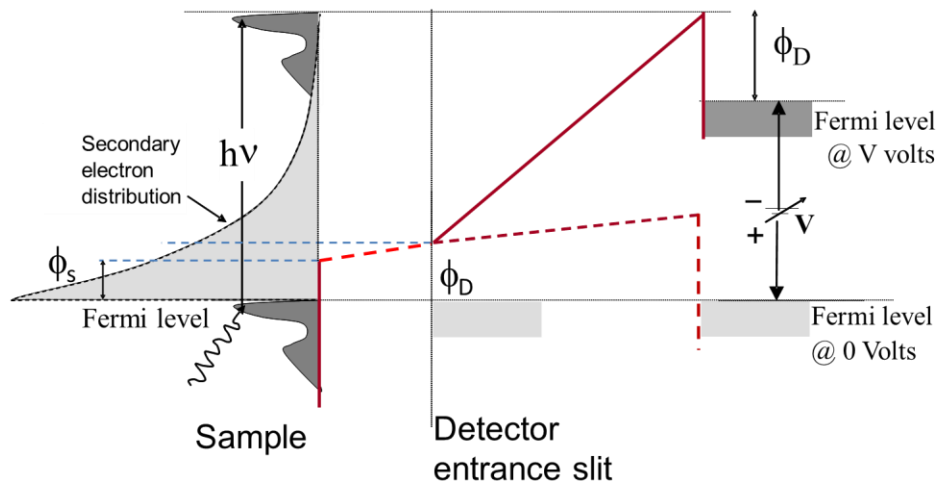
The highest kinetic energy corresponds to electrons emitted from the Fermi edge:  $E_{kin,F} = h\nu - \phi$ . The lowest kinetic energy electrons ( $E_{kin} = 0$ ) are those that emerge with the energy of the vacuum level. These electrons are secondary electrons generated in a cascade process where higher energy photoelectrons loose energy by exciting electrons from states below the Fermi level to empty states above it. In this process the number of electrons keeps increasing as inelastic collisions occur during transport to the surface while the number of these lower energy electrons is increasing geometrically at lower and lower energies. The work function is the cut-off energy for escaping into the vacuum.

It is important to keep in mind that the energy of the emitted electrons is measured by some energy analyzer, with an entrance slit usually at ground potential, and are then deflected and steered to a detector by application of a suitable voltage. For example a repelling grid or small aperture that admits electrons of a given energy determined by a negative bias applied to it. The energy diagram of the figure illustrates the relation between applied bias to the analyzer  $V$ , kinetic energy of the electrons and work functions:

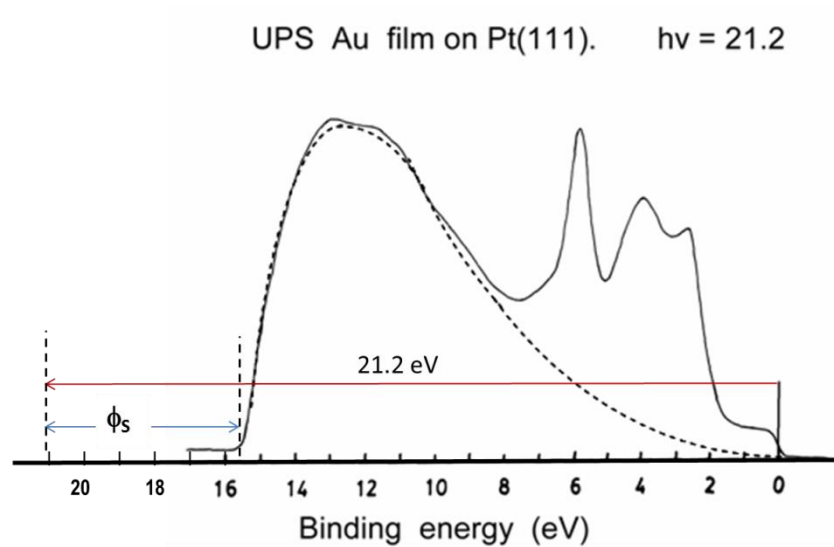
The following relations can be easily derived for electrons emitted from the Fermi level:

$$\begin{aligned} E_{kin}^{outside\ sample} &= h\nu - \phi_S \\ E_{kin}^{detector} &= h\nu - \phi_D ; h\nu = eV + \phi_D \end{aligned}$$

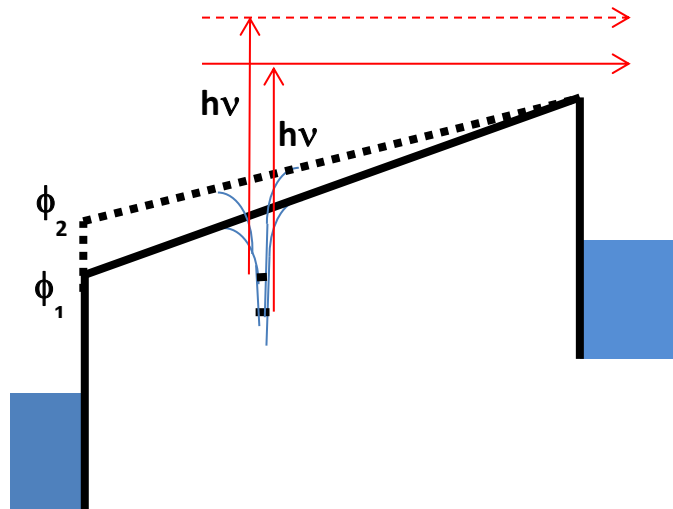
The value of  $\phi_S$  can be obtained from a photoelectron emission experiment by subtracting from  $h\nu$  the width of the measured energy spectrum. Notice however that the kinetic energy of the emitted electrons can be different just outside the sample and inside the analyzer if the work functions are different.



For example, the photoelectron emission spectrum of a gold film on Pt(111) shown in the figure was obtained using He-I line photons at 21.2 eV. The smooth broken line represents the secondary electron distribution. As customary in such experiments, the zero of the energy scale is set at the Fermi level (vertical line at  $E=0$ ). Since the width of the energy distribution is 15.5 eV, we obtain  $\phi_{\text{Au}} = 21.2 - 15.5 = 5.7$  eV.



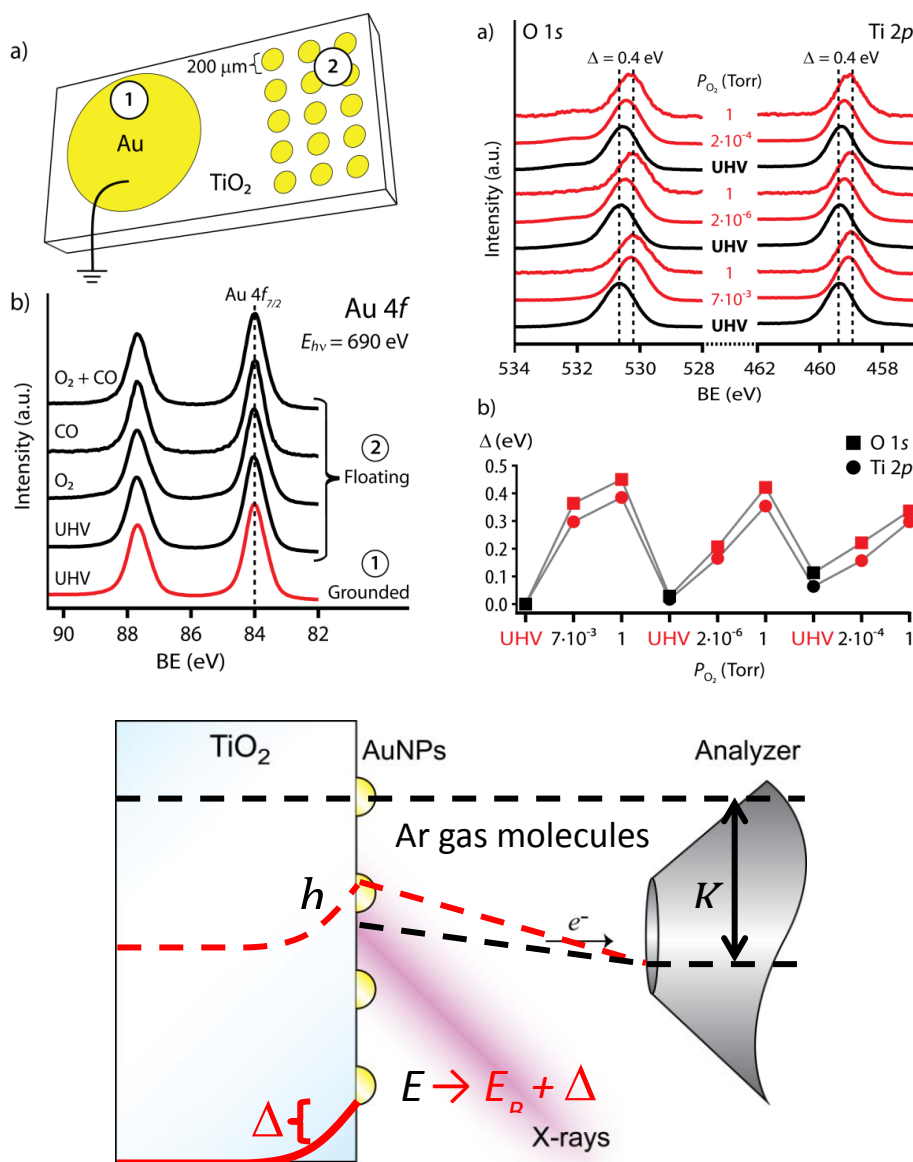
If the work function of the sample changes, for example because gases adsorb on its surface, then the molecules in the gas phase near the sample will appear with different kinetic energies, and the shift can be used to measure the changes in work function.



This can be used also to measure changes in band bending in semiconductors.

Example:

A controversy existed in the research literature on whether Au deposited on  $\text{TiO}_2$  gets oxidized by exposure to oxygen. XPS was used to sort out this point. If Au oxidized and reduced its core level peaks would shift to higher or lower energy. The problem arose because to calibrate the energy scale the XPS peaks of O and Ti were used as a reference, i.e., assume to be of fixed energy. However we showed that this is not the case, and it is the Au that remains at fixed energy, while the O and Ti peaks shift BUT THE SHIFT IS DUE TO BAND BENDING THAT CHANGES THE VACUUM LEVEL OF THE  $\text{TiO}_2$  SAMPLE:



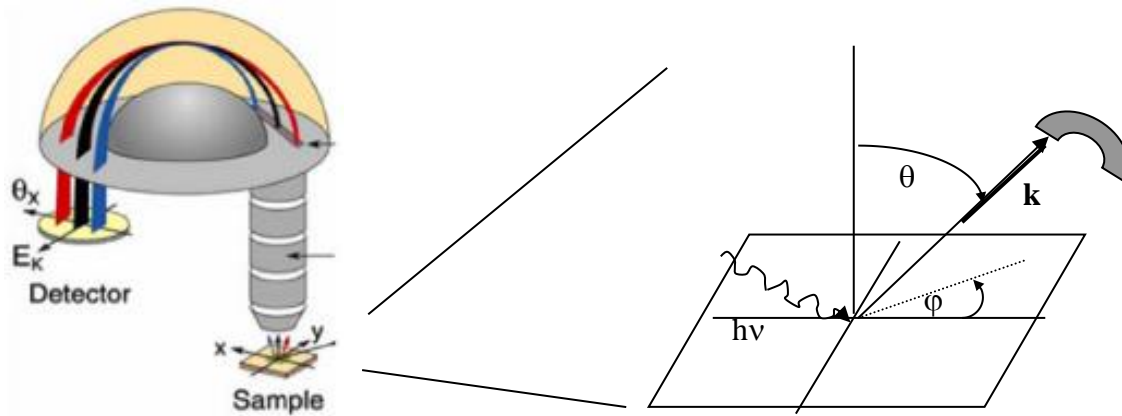
For more details see:

[Charge state of  \$\text{TiO}\_2\$  supported Au nanoparticles at high  \$\text{O}\_2\$  pressure](#)

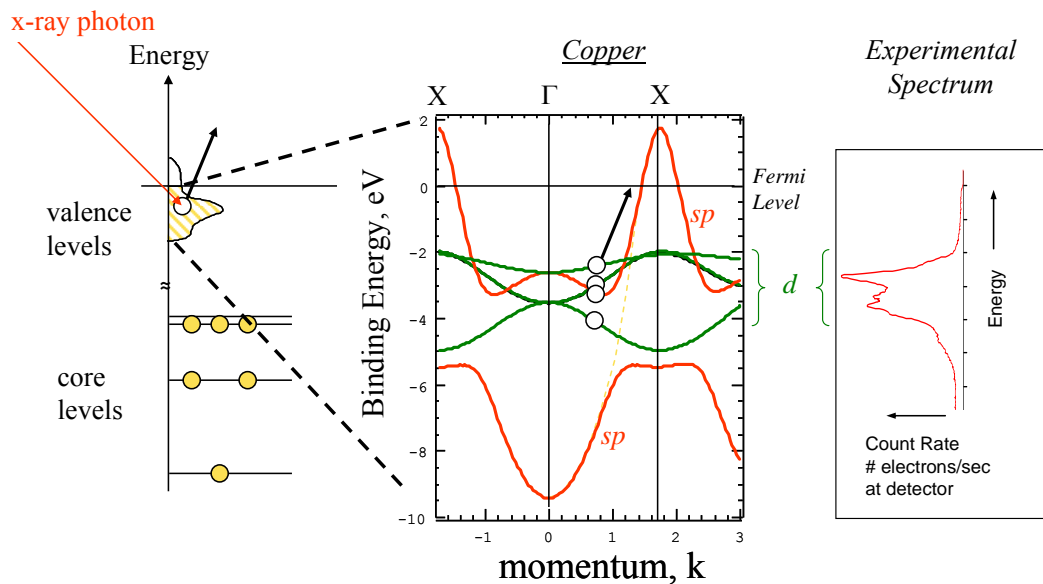
Soeren Porsgaard, Peng Jiang, Ferenc Borondics, Stefan Wendt, Hendrik Bluhm, Flemming Besenbacher, Miquel Salmeron. *Angewandte Chemie Intl.* **123**, 2266-2269 (2011).

## Studies of band structure using angle resolved photoemission (ARPES)

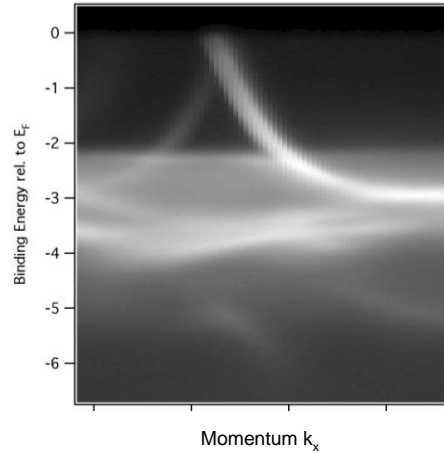
Angle Resolved Photoelectron Spectroscopy (ARPES) is today the most powerful tool to investigate the electronic structure of materials, because it makes possible to measure the energy dispersion,  $E(\mathbf{k})$ , of electrons in the various energy bands by measuring the energy of the photoemitted electrons at specific azimuthal and polar angles, as shown in the schematic.



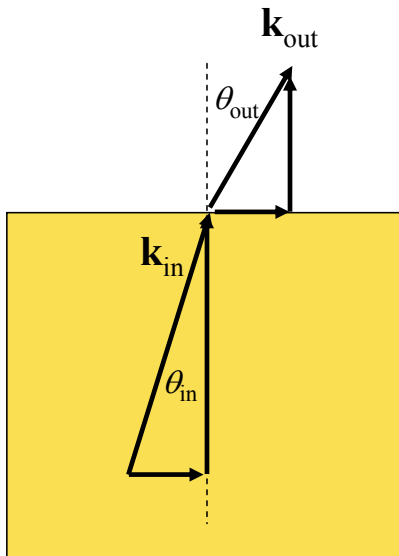
If, as shown in the figure below, there is a peak in the energy distribution of photoemitted electrons with kinetic energy  $E_{\text{kin}}$ , this peak corresponds to one electronic state with momentum  $\mathbf{k}$  that is determined by the at polar and azimuthal angles  $\theta$  and  $\phi$ , where with the detector is placed. We obtain the binding energy through:  $E_{\text{kin}} = h\nu - E_{\text{binding}} - \phi$ , ( $\phi$  = work function of the sample). From  $E_{\text{kin}}$  we obtain  $k = \sqrt{2m/h^2}$ .



In this manner, by obtaining  $E$  for each value of  $\theta$  and  $\phi$ , one can construct the band structure. If the detector permits both energy and angular dispersion, as in modern hemispherical analyzers like the one shown schematically above, then a channel plate produces directly a slice of the 3D  $E(\mathbf{k})$  curve, as in the example shown below from Cu(100) obtained at the ALS in the Lawrence Berkeley Laboratory.



To determine the wavevector inside the solid we need to be careful with the refraction across the surface. The components in vacuum are:  $k_x = k \cdot \sin(\theta) \cdot \cos(\phi)$ , and  $k_y = k \cdot \sin(\theta) \cdot \sin(\phi)$ . These two components ( $k_{\parallel}$ ) are conserved across the interface. The normal component  $k_z$  however is not the same outside and inside the sample  $k_z^i > k_z$ . This is because of the crystal potential, i.e., the energy from the bottom of the conduction band to the vacuum level ( $= E_F + \phi$ ) is added to  $\hbar^2 k_z^2 / 2m$ .



### **Kinematic relations**

$$E_{kinetic} = \hbar \nu - E$$

$$k_{out} = \sqrt{\frac{2m}{\hbar^2} E_{kin}}$$

$$k_{in} = \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

$$k_{out,\parallel} = k_{in,\parallel} \equiv k_{\parallel}$$

### **“Snell’s Law”**

$$k_{\parallel} = \sin \theta_{out} \sqrt{\frac{2m}{\hbar^2} E_{kin}} = \sin \theta_{in} \sqrt{\frac{2m}{\hbar^2} (E_{kin} + V_0)}$$

### **Critical angle for emission**

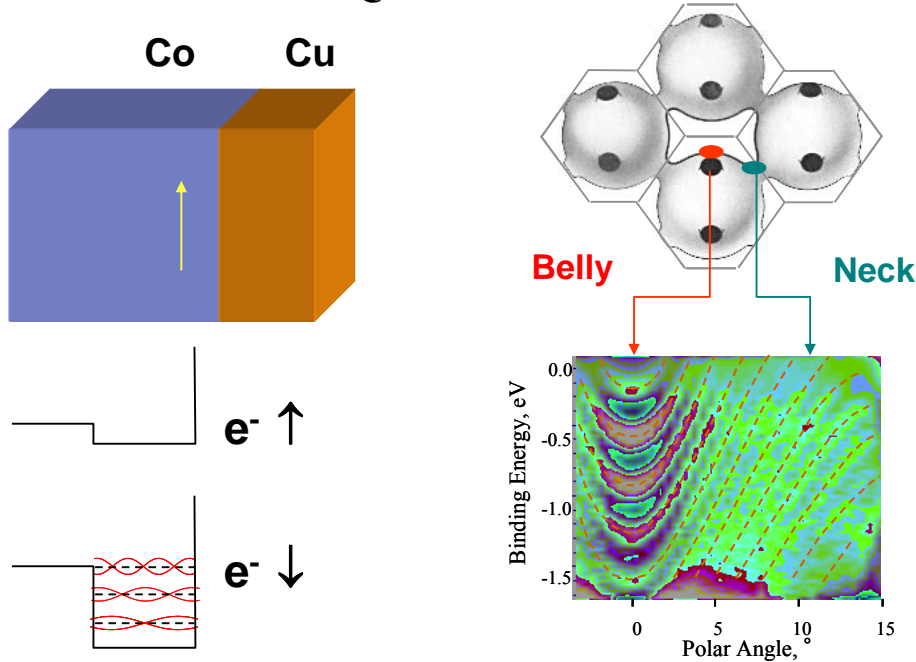
$$(\sin \theta_{in})_{max} = \sqrt{\frac{E_{kin}}{E_{kin} + V_0}}$$



### Photoemission from surface states

Surface states are gap states, i.e., forbidden in the bulk. The  $k_z$  component of the momentum is imaginary so that the amplitude of the wavefunction decays exponentially away from the surface. The only dispersion is in  $k_x$  and  $k_y$  so that the  $E(k_x) \propto k_x^2$ . Other confined states are bulk allowed states in thin films. See electron in a box chapter above. Below is an example from Cu on Co:

## Surface and Quantum-confined states



J. Unguris et al, PRL 67,140 (1991).  
P. Segovia et al, PRL 77,3455 (1996)

Data from  
Kawakami Thesis, UCB

STM images of Cu(111) at 4K obtained by Aitor Mugarza and Tomoko Shimizu in my laboratory. Cu has a band gap along the [111] direction. The top image shows the standing waves created by the electrons in the surface states of the Cu(111) surface.

The standing waves originate from the reflections on the two parallel steps (only one visible). The second image shows an expanded view, with waves forming rings around impurities. The Cu atoms are visible forming a compact hexagonal network in the background

